

# A note on the critical nuclear charge that binds $N$ electrons

Gabriel Gil and Augusto González

*Instituto de Cibernética, Matemática y Física, Calle E 309, Vedado, Ciudad Habana, Cuba*

The critical charge,  $Z_c$  that binds  $N$  electrons in an atom is known to satisfy the relation,  $Z_c = N - 1 - \delta$ . Numerical calculations show that  $\delta$  exhibits a correlation with the electron affinity,  $E_a$ , of the neutral atom with  $N - 1$  electrons, and that  $\delta < 0.48$  for  $N < 90$ . We re-examined  $Z_c$  by means of a very simple model that treats the interaction of the outermost electron with the core electrons through a zero-range force theory, whereas the residual Coulomb interaction is included in first-order perturbation theory. The relation,  $\delta = 0.836 \sqrt{E_a}$ , coming from our model, is fairly well observed by the computed  $\delta$  and the experimental  $E_a$ .

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## I. INTRODUCTION

Qualitative understanding of phenomena come from very simple models that capture their essence. In atoms, perhaps the most successful simple models are the famous Thomas-Fermi (TF) Theory<sup>1,2</sup>, and the large- $D$  expansion<sup>3</sup>, leading, the latter, to a qualitative picture similar to the one devised by Lewis long ago<sup>4</sup>.

The theory by Thomas and Fermi is a mean-field one in which the scaling properties of the kinetic energy and Coulomb potentials are apparent. This fact leads to a universal relation for the energy of the atom with  $N$  electrons and charge  $Z$ ,<sup>2</sup>  $E_{TF}(N, Z) = N^{7/3} f(N/Z)$ , or for the ionization potential<sup>5</sup>,  $I_p(N, Z) = N^{4/3} g(N/Z)$ , where the universal functions  $f$  and  $g$  depend only on the combination  $N/Z$ .

For a fixed ratio  $N/Z$ , the ionization potential (or the electron affinity,  $E_a$ ) should behave as  $E_a \sim N^{4/3}$ , when  $N$  increases. This dependence holds extremely well for cations ( $N < Z$ ), even for small  $N$  values, as can be seen in the upper panel of Fig. 1, but breaks down for neutral atoms ( $N = Z$ ), where  $I_p$  or  $E_a$ , apart from fluctuations due to shell effects, take roughly a constant value (Fig. 1, lower panel).

The reason for such a breaking down of TF predictions for neutral atoms, in certain situations, is the proximity of the anionic instability threshold, that is, the fact that atoms become unstable when  $Z < Z_c \lesssim N - 1$ .

Rigorous bounds for the critical nuclear charge,  $Z_c$ , that binds  $N$  electrons have proven to be of little use<sup>8</sup>. Numerical computations for atoms with up to 89 electrons<sup>9,10</sup>, on the other hand, lead to:

$$Z_c = N - 1 - \delta, \quad (1)$$

where the magnitude  $\delta < 0.48$  shows a correlation with the electron affinity of the neutral atom with  $N - 1$  electrons.

In the present paper, we use a very simple model, similar in spirit to the one used in Refs. [10], from which we obtain (in atomic units):

$$\delta = 0.836 \sqrt{E_a}. \quad (2)$$

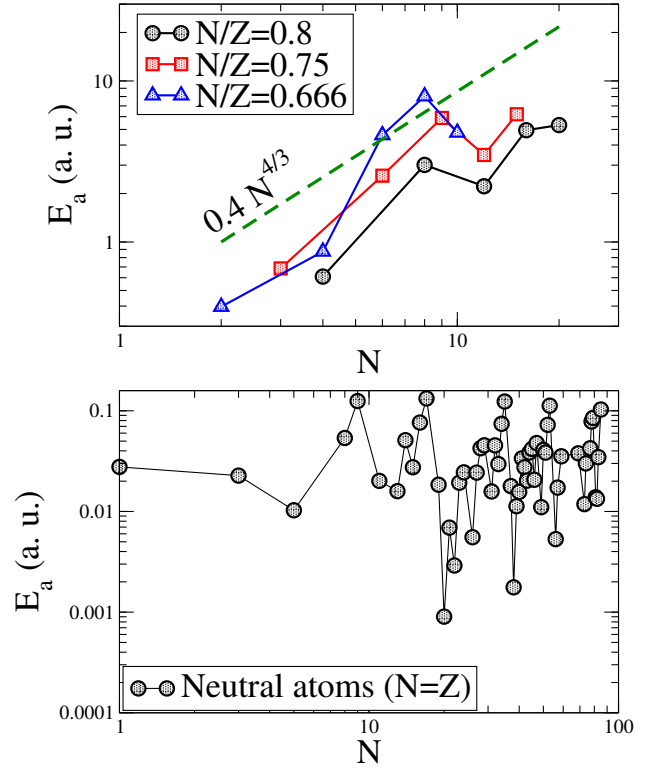


FIG. 1: (Color online) Upper panel: Electron affinities of cations with  $N \leq 20$  and fixed  $N/Z$  ratios. Data are taken from the NIST database<sup>6</sup>. The line  $0.4 N^{4/3}$  is drawn as a reference for the slope. Lower panel: Electron affinities of neutral atoms<sup>7</sup>.

Relation (2) is fairly well observed by the calculated  $\delta$  when the experimental  $E_a$  of the neutral atoms with  $N - 1$  electrons are introduced, as shown in Fig. 2.

## II. THE MODEL

When  $Z \approx N - 1$ , we may use a very simple model to get reasonable results. The interaction of the outermost electron with the neutral core is described by a square

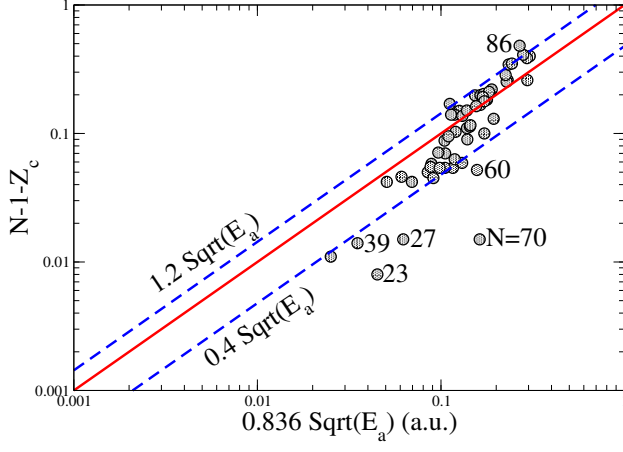


FIG. 2: (Color online) Computed values of  $\delta^{9,10}$  versus the square root of the experimental electron affinity for the neutral atom with  $N - 1$  electrons<sup>7</sup>. The central line is our prediction, Eq. (2)

well potential of depth  $V$  and radius  $R$ .  $V$  and  $R$  enter in a combination such that the binding energy of the electron is  $E_a$ .

At this level, the parameter  $R$  is not determined, as in a theory with zero-range forces<sup>11</sup>, and the details of the potential for  $r < R$  are not important. The only magnitude that matters is  $E_a$ , which determines the wave function in the outer region:

$$\psi \sim \sqrt{2\kappa} \frac{\exp(-\kappa r)}{r}, \quad (3)$$

where  $\kappa = \sqrt{2E_a}$ . This function can be used to perturbatively compute the contribution to the energy coming from the Coulomb interaction with the almost neutral core:

$$\begin{aligned} \Delta E &= (N - 1 - Z) 2\kappa \int_R^\infty \frac{dr}{r} \exp(-2\kappa r) \\ &= (N - 1 - Z) \sqrt{E_a} F(\sqrt{E_a} R), \end{aligned} \quad (4)$$

where the explicit expression  $F(x) = 2\sqrt{2}(\ln 1/(2\sqrt{2}x) - 0.5772) + 8x$  comes from the assumption that  $1/\kappa$  should be greater than the radius  $R$ .

The energy of the anion with  $N$  electrons and charge  $Z \approx N - 1$  is, thus:

$$E = -E_a + (N - 1 - Z) \sqrt{E_a} F(\sqrt{E_a} R). \quad (5)$$

We may use the freedom left in the definition of the parameter  $R$  in order to minimize the energy. It may be seen that  $F$  takes a minimum value, 1.196, when  $R = 0.35/\sqrt{E_a}$  (Fig. 2, upper panel).

When  $E_a$  is small enough, one may expect that the slope of the energy curve at  $Z = N - 1$ , i. e.  $-1.2 \sqrt{E_a}$ ,

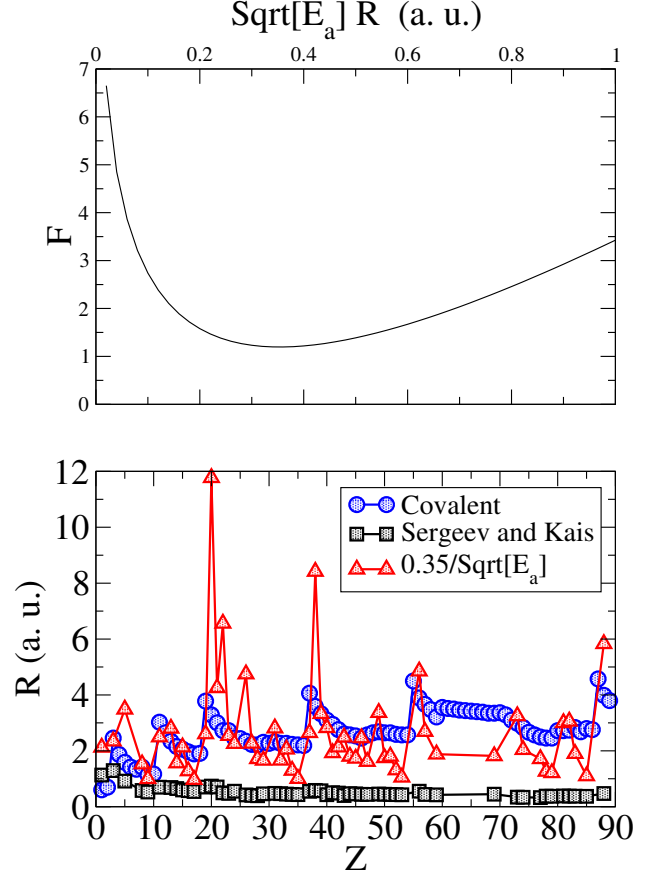


FIG. 3: (Color online) Upper panel: The function  $F$  entering Eq. (4). It is computed in lowest order, up to terms linear in  $\sqrt{E_a} R$ . Lower panel: Comparison between the values taken by the parameter  $R = 0.35/\sqrt{E_a}$ , the covalent radius, and the radius used by Kais and co-workers<sup>10</sup> for the neutral atom with  $N - 1$  electrons.

is practically the same as the slope computed at  $Z_c$ . The linear behaviour at  $Z_c$  was demonstrated in Ref. [12]. Thus, we may use this slope to estimate  $Z_c$ , leading to the expression for  $\delta$  given in Eq. (2) of section I.

### III. DISCUSSION

We put together in Fig. 2 the computed values of  $\delta^{9,10}$  and the experimental  $E_a$ <sup>7</sup>. Most of the points are grouped around the line given by Eq. (2). There are, however, a few exceptions that we want to comment. They may correspond to inconsistencies in the computed  $\delta$  or the measured  $E_a$ .

The point with  $N = 86$  is the only one for which  $E_a$  is not measured, but computed<sup>13</sup>. The reported electron affinity of At seems to be underestimated.

The points with  $N = 60$  and  $70$  are related to the  $E_a$  of Pr and Tm, respectively. Both measurements were performed by the same group using the same experimen-

tal setup<sup>14</sup>. The authors stress that the reported values, around 1 eV, are much higher than the theoretical estimates<sup>15</sup>, around 0.1 eV. We notice that a value of 0.1 eV is more consistent with our prediction.

On the other hand, the  $E_a$  of Fe and Ti enter the points in the Figure labelled as  $N = 27$  and 23. We notice that there is also a small difference between measured<sup>16</sup> and theoretical<sup>17</sup> values. The latter are closer to our curve.

Let us stress that the radius  $R = 0.35/\sqrt{E_a}$  takes values in between the covalent radius and the radius used by Kais and co-workers<sup>10</sup> for the neutral atom with  $N - 1$  electrons, as shown in Fig. 3, lower panel. The exceptions are the systems with very low  $E_a$ , for which  $R$  becomes higher than the covalent radius. The magnitude  $R$  is simply a parameter in our model, not directly related to the real potential that experiences the electron. It is remarkable that the theory, in the  $\kappa R \rightarrow 0$  limit, assigns to  $R$  “reasonable” values.

#### IV. CONCLUSIONS

We use a kind of “zero-range force theory” in order to compute, for the atom with  $N$  electrons and charge

$Z$ , the slope of the curve  $E$  vs  $Z$  at the point where  $Z = N - 1$ . The obtained slope,  $1.2 \sqrt{E_a}$ , allows us to estimate the critical charge for binding  $N$  electrons,  $Z_c = N - 1 - 0.836\sqrt{E_a}$ . Comparison between the computed  $Z_c$  and measured  $E_a$  shows that this simple relation holds. Some points lying far from the curve are characterized by discrepancies between the experimental and theoretical values for  $E_a$ .

The case  $E_a = 0$ ,  $Z_c = N - 1$  is also contained in our curve. There is an additional property of the energy curve in this situation. Due to the fact that it is precisely the residual Coulomb interaction which binds the electron, the energy should behave as:  $E \sim -(Z - N + 1)^2$ , for  $Z$  close enough to  $N - 1$ . We did not find computed data to check this behaviour.

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